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(54) Title: HYPERBRANCHED POLYESTER AND A PROCESS FOR ITS PREPARATION

(57) Abstract

The invention relates to a hyperbranched polymer comprising a nucleus and polyol and polycarboxy residues, the hyperbranched polymer having at least 6 terminal hydroxyl- or carboxyl groups and a Carothers gel point lower than 1. The hyperbranched polymer having at least 6 terminal hydroxyl- or carboxyl groups, is obtainable by starting with a nucleus compound containing at least one hydroxyl group as the nucleus and reacting it with a compound containing at least one anhydride group, after which the resulting first generation acid-terminated addition product is reacted with a compound containing at least one epoxy group; the resulting first generation hydroxyl-terminated addition product thereafter is reacted, in the second generation, with a compound containing at least one anhydride group, after which the resulting second generation acid-terminated addition product, is reacted with a compound containing at least one epoxy group, resulting in a second generation hydroxyl-terminated addition product, and in at least one generation monomers are used that have at least one functional group besides the anhydride group or epoxy group.

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HYPERBRANCHED POLYESTER AND A PROCESS FOR ITS PREPARATION.

The invention relates to a hyperbranched polymer
and a process for the preparation of a hyperbranched poly-
5 mer.

Hyperbranched polymers are often referred to as
"dendrimers" in the literature (see, for example,
Encyclopedia of Polymer Science and Engineering, Index
Volume, 1990, pp. 46-92).

10 Hyperbranched polymers (dendrimers) are
three-dimensional, highly ordered oligomeric and polymeric
molecules with a good defined chemical structure. These
dendrimers differ from classical oligomers and polymers by
their extraordinary symmetry, high branching and maximized

15 terminal functionality density. They are formed from a
functional core (nucleus) surrounded by a plurality of
layers of branched structural units. The plurality of layers
around the nucleus are called generations and in each
generation the functionality of the macromolecule multiplies

20 with the degree of branching of the structural units used.
The resulting dendrimers have a tree-like structure (Greek:
"dendrites") within ball-shaped macromolecules having a very
high functionality and a very narrow molecular weight dis-
tribution. Such highly branched and highly functional

25 macromolecules cannot be prepared by the conventional
processes for making normal branched polymers because they
would result in broad molecular weight distributions and in
macroscopic gelling of the system.

In the article "One-step synthesis of hyperbranched
30 dendritic polyesters" (J. Am. Soc. 1991, 113, 4583-4588),
Hawker, Lee and Frechet describe hyperbranched polyesters.

Hawker et al. describe a synthesis of hyperbranched
polyesters starting from dihydroxybenzoicacid which is

reacted with trimethylsilyl chloride and thionyl chloride to
give di-trimethylsiloxybenzoyl chloride, after which the

5 hyperbranched polyester is formed by means of a one-step
synthesis.

The Hawker process has many disadvantages. The
process cannot be used on an industrial scale because of the
reactants used, such as, for example, trimethylsilyl

10 chloride, thionyl chloride and benzoyl chloride, and because
of the process stages such as the solvent process and the
purification step. In particular, the large quantities of
solvent which have to be distilled off make the process
unattractive.

15 Another disadvantage of the Hawker process is the
limited freedom of choice in the composition of the monomers
to be used. This process consequently leads only to purely
aromatic polyesters. However, in order to obtain a good
balance in mechanical properties it must be possible to vary

20 the starting materials, such as aromatic and (cyclo)alipha-
tic monomers.

An object of the invention is to provide hyper-
branched polymers. Another objective of the invention is to
provide an industrially readily useable process for the

25 preparation of these hyperbranched polymers, which avoids
the disadvantages and problems of conventional processes
described above. A further objective of the invention is to
provide a coating composition containing the hyperbranched
polymers.

30 The hyperbranched polymer according to the
invention is characterized in that it comprises a nucleus
and polyol and polycarboxy residues the hyperbranched
polymer having at least 6 terminal hydroxyl- or carboxyl
groups and a Carothers gelpoint lower than 1.

35 Preferably the hyperbranched polymer has at least 8
terminal hydroxyl- or carboxyl groups; more preferably at
least 10.

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The gelpoint according to the Carothers equation,
being the theoretical conversion factor at which the polymer
5   tends to gelate, preferably is lower than 0.95; more
preferably lower than 0.90. The Carothers equation has been
disclosed by G. Odian, Principles of polymerization, J.
Wiley & Sons (1981), p. 113-116. Surprisingly, it has been
found, that - although all the addition reactions almost
10   have a conversion factor of 1 - no gelation takes place.

The hyperbranced polymers according the invention
have in general a relatively low polydispersity. The
polydispersity of linear polyesters is about 2. Branched
polyesters -made via direct and transesterification methods-
15   in general have very much higher polydispersities. In
contrast, the polymers according the invention in general
have a low polydispersity although it may steadily increase
with (very) high branching. In case the nucleus has a
polydispersity of 1, than the polydispersity of the polymer
20   can be dipicted by the following formula:
D/[no.generations]<2. Preferably D/[no.generations]<1.8. In
case the nucleus has a polydispersity higher than 1, the
figure has to be multiplied with the dispersity of the
nucleus.
25   The hyperbranched polymer is obtainable by starting
with a nucleus compound containing at least one hydroxyl
group and reacting it with a compound containing at least
one anhydride group, after which the resulting
first-generation acid-terminated addition product is reacted
30   with a compound containing at least one epoxy group; the
resulting first-generation hydroxyl-terminated addition
product thereafter is reacted, in the second generation,
with a compound containing at least one anhydride group,
after which the resulting second-generation acid-terminated
35   addition product is reacted with a compound containing at
least one epoxy group, resulting in a second-generation
hydroxyl-terminated addition product whereby in at least one
generation monomers are used that have at least one
functional group besides the anhydride group or epoxy group.

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Both the addition reactions are repeated
alternatively in order to obtain a hyperbranched polymer of
5   the generation that is desired. Each generation step
increases the molecular weight of the resulting
hyperbranched polymer.

The reaction mechanisms in the subsequent
generations are identical with those in the second
10   generation.

The abovementioned nucleus with hydroxyl groups is
regarded for the sole purpose of definition as being of
generation zero; the first acid-terminated and
hydroxyl-terminated addition products are of generation one;
15   the second acid-terminated and hydroxyl-terminated addition
products are of generation two, etc. Generally, the obtained
hyperbranched polymer has 1-20 generations; preferably 2 or
more generations and very preferably 3-10 generations.

The nucleus, which can be a monomeric, oligomeric
20   or polymeric compound, contains at least one hydroxyl group.
Preferably, the nucleus contains 1-10 hydroxyl groups; more
preferably this is 2-8.

If required, the nucleus can be formed by the
addition reaction of a compound containing at least one
25   carboxyl group and a compound containing at least one epoxy
group, resulting in a hydroxyl-terminated addition product.

Furthermore, a hydroxyl functional nucleus can be
made —in case of oligomers or polymers— by well known
esterification methods, urethane oligo- and polymerisation,
30   radical polymerisation and the like.

Mostly, the quantities of the added reactants are
chosen in such a way, that substantially all terminal
hydroxyl groups or acid groups of the nucleus or the
respective addition products can react. Therefore, the
35   reactants are added in at least about an equimolar amount.
Thus, the molar ratio between the terminal hydroxyl groups
and the anhydride group containing compounds or between the
terminal acid groups and the epoxy group containing
compounds in all the reactions mentioned are about 1.1:0.9

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to 0.9:100; preferably 1.1:0.09 to 0.9:10; more preferably
1.1:0.9 to 0.9:1.1. Most preferably the molar ratios are
5   about 1:1, since at that moment extra purification steps are
avoided.

The reaction temperatures can be chosen in a broad
range. The reaction in all steps is usually carried out
below 200°C, preferably below 180°C to avoid side reactions.
10 In order to obtain a good balance between reaction rates and
reduction of side reactions, the reactions preferably are
carried out at temperatures of between 80°C and 160°C.

Suitable compounds containing at least one hydroxyl
group useful for being comprised in the nucleus are, for
15 example: glycols, for example 2,2,4-trimethyl-1,3-
pentanediol, cyclo-hexane dimethanol, dipropyleneglycol,
neopentyl glycol, 1,4-butanediol, 1,3-butanediol, 1,6-
hexanediol or 1,8-octanediol; triols, for example glycerol,
trimethylolethane and trimethylolpropane; polyols, for
20 example ditrimethylolpropane, pentaerythritol,
di-pentaerythritol or sorbitol; and low molecular polyesters
or polyurethanes having a molecular weight of, for example,
about 3000. Other useful oligomers are e.g.
polyethyleneglycol, polypropyleneglycol, monoalkylethers of
25 polyethylene- or polypropyleneglycol, and alkoxylated
bisphenol-A, such as with 2-12 units ethoxylated or
propoxylated bisphenol, and the corresponding hydrogenated
compounds.

Preferably, low molecular weight polyols are used
30 as the compound containing hydroxyl groups.

Suitable compounds containing at least one epoxy
group (useful in making the nucleus and in making the
generations) are, for example: monoepoxides, for example:
monocarboxylicacidglycidylester (Cardura E10R; Shell),
35 ethylene oxide, propylene oxide or phenyl glycidyl ether;
hydroxyepoxides such as the glycidylester of hydroxypivalic
acid, of hydroxybutyric acid, or of hydroxystearic acid;
diepoxides, for example diglycidylterephthalate, bisphenol

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A based epoxyresins; diglycidyl ethers, for example: 1,6-
hexanediol diglycidyl ether; or triepoxides, for example:
5   trimethylolpropane triglycidyl ether,
triglycidylisocyanurate, trimethylolethane triglycidyl
ether, the polyglycidyl ether of castor oil. In case
polyepoxides are used in the addition reactions of the
generations building, it is preferred to have, after the
10   addition reaction, a reaction that opens the remaining epoxy
groups, e.g. a reaction with water.
Preferably, monoepoxides are used in the generation
building, more preferably, Cardura E10^R and/or propylene
oxide are used.
15   Suitable compounds containing at least one carboxyl
group are, for example, acid-terminated polyesters
polyethers or polyurethanes, dicarboxylic acids, for example
isophthalicacid, terephthalicacid, adipicacid and for
example trimelliticacid.
20   Suitable compounds containing at least one
anhydride group are, for example, trimelliticacidanhydride,
succinicacidanhydride, pyromelliticacidanhydride, maleic-
acidanhydride, succinicacidanhydride, phthalicacidanhydride,
tetrahydrophthalicacidanhydride, hexahydrophthalicacid-
25   anhydride, butanesuccinicacidanhydride, glutaricacid-
anhydride and itaconicacidanhydride. In case polyacid-
anhydrides are used in the addition reactions of the
generations building, it is preferred to have, after the
addition reaction, a reaction that opens the remaining
30   anhydride groups, e.g. a reaction with water.
Preferably, trimelliticacidanhydride is used as the
compound containing anhydride groups for the generation
building.
Suitable solvents are, for example, toluene,
35   benzene, aceton, ethyleneglycolmonobutyletheracetate,
.n-methylpyrrolidine, methylisobutylketone,
methylethylketone, xylene and propyleneglycolmonomethyl-
etheracetate. If required, a mixture of solvents can be

used. Preferably, methylisobutylketone is used as the
solvent.

5   Suitable catalysts in the preparation of the
hyperbranched polymer are, for example, tertiary amines,
phosphonium salts and metal tin compounds. Suitable tertiary
amines are e.g. dimethylbenzylamine, dimethylaminopyridine
and dimethylethanolamine. Suitable phosphonium salts are
10 e.g. trifenylethylphosphoniumbromide and
trifenylmethylphosphoniumchloride. Suitable metal tin
compounds are e.g. dibutyltinoxide, dibutyltinlaureate and
dibutylhydroxytinchloride. If required the addition
reactions can be carried out without adding a catalyst.
15   Of course, it is possible to have urethane groups
built in via chain lengthening reactions, or by the use of
oligourethanes with anhydride or epoxy functionality.
       The process can be readily used industrially and
has the further advantage that there is large freedom in the
20 choice of the monomeric composition for the hyperbranched
polymer. The successive generations can be built up from the
same monomeric building-blocks in each generation, but -if
required- it is also possible to use various monomeric
building-blocks in distinct successive generations. Using
25 this process has the advantage of a large freedom in
choosing these building blocks. Thus it is possible, for
example, to use only aromatic compounds, such as, for
example, trimelliticacidanhydride and phenyl glycidyl ether
in the first generations, and to use combinations of
30 aliphatic and aromatic compounds in the outermost genera-
tions, as a result of which a macromolecule with a hard core
and a soft shell results. This principle can also be
employed in reverse. This results in a hyperbranched
polymer, such as, for example, a hyperbranched polyester,
35 having a core-shell structure.
       The hyperbranched polyester as a rule has at least
6 branches, and hence, at least 6 functional groups.
Preferably, the polymer has at least 10 branches or 10
functional groups. The initial functional groups are either

hydroxy or carboxy. These groups may be modified (if
required, only partly) by methods known per se, as long as
5   the temperature applied during these reactions does not
allow substantial transesterification. Hence, as a rule, the
temperature should remain below 180°C. For instance, acid
groups may be neutralised with amines, metal hydroxides,
yielding a water dispersable hyperbranched polymer. Also the
10   acid groups can be reacted with a (large) excess of diepoxy
as to make an epoxy functional hyperbranched polymer. A
hydroxy-functional polymer may be modified e.g. with a
(large) excess of di-isocyanate to make an isocyanate
functional dendrimer. Such an isocyanate functional dedrimer
15   may e.g. be modified with hydroxyethyl(meth)acrylate to make
UV curable coatings.

        The advantage of the hyperbranched polyesters is
that they have a very high molecular weight coupled with a
very low viscosity. As a result, they are very suitable for
20   use in coating compositions in order to increase the solids
contents.

        The invention is explained in more detail with
reference to the examples which follow, without, however,
being restricted thereto.
25

<u>Examples</u>
<u>Examples I-IV</u>
<u>Preparation of hyperbranched polyester</u>

30   <u>Example I</u> (1st generation)
        In a 3-litre reaction flask having a mechanical
stirrer and a thermometer, 67 grams of trimethylolpropane
(0.5 mol), 288 grams of trimelliticacidanhydride (1.5 mol)
and 410 grams of propyleneglycolmonomethyletheracetate were
35   warmed to 150°C under a constant stream of nitrogen, after
which the temperature was kept at 150°C for 30 minutes.
After cooling to 120°C, 750 grams of monocarboxylic
acidglycidylester (Cardura E10ᴿ from Shell) (3.0 mol) and

0.1% by weight of triphenylethylphosphoniumbromide were
added, with the temperature being kept below 155°C. After
5   the acid number had fallen to less than 3 mg of KOH/gram of
resin, the resin was cooled.

Viscosity according to the falling ball method: 5.5
dPa.s (65% solid in propylene glycol monomethyl ether
acetate, 23°C). Carothers gel point (PC) = 0.833.
10

Example II (2nd generation)

In a 3-litre reaction flask having a mechanical
stirrer and a thermometer, 557 grams of the product (0.184
mol of solid resin) obtained from generation 1 and 212 grams
15   of trimelliticacidanhydride (1.104 mol) were warmed to 150°C
under a constant stream of nitrogen, after which the
temperature was kept at 150°C for 30 minutes. After cooling
to 120°C, 552 grams of monocarboxylicacidglycidylester
(Cardura E10^R from Shell) (2.208 mol) and 0.1% by weight of
20   triphenylethylphosphonium bromide were added, with the
temperature being kept below 155°C. After the acid number
had fallen to less than 3 mg of KOH/gram of resin, the resin
was cooled.

Viscosity according to the falling ball method: 11
25   dPa.s (65% solid in propyleneglycolmonomethyletheracetate,
23°C) (PC) = 0.847.

Example III (3rd generation)

In a 3-litre reaction flask having a mechanical
30   stirrer and a thermometer, 553 grams of the product (0.077
mol of solid resin) obtained in generation 2, 177 grams of
trimelliticacidanhydride (0.924 mol) and 170 grams of
propyleneglycolmonomethyletheracetate were warmed to 150°C
under a constant stream of nitrogen, after which the
35   temperature was kept at 150°C for 30 minutes. After cooling
to 120°C, 462 grams of monocarboxylicacidglycidylester
(Cardura E10^R from Shell) (1.848 mol) and 0.1% by weight of
triphenylethylphosphoniumbromide were added, with the
temperature being kept below 155°C. After the acid number

had fallen to less than 3 mg of KOH/gram of resin, the resin was cooled.

5   Viscosity according to the falling ball method: 21.5 dPa.s (65% solid in propyleneglycolmonomethylether acetate, 23°C). (PC) = 0.854.

Example IV (4th generation)

10   In a 3-litre reaction flask having a mechanical stirrer and a thermometer, 621 grams of the product (0.035 mol of solid resin) obtained in generation 3, 161 grams of trimelliticacidanhydride (0.840 mol) and 122 grams of propyleneglycolmonomethyletheracetate were warmed to 150°C

15   under a constant stream of nitrogen, after which the temperature was kept at 150°C for 30 minutes. After cooling to 120°C, 420 grams of monocarboxylicacidglycidylester (Cardura E10^R from Shell) (1.680 mol) and 0.1% by weight of triphenylethylphosphoniumbromide were added, with the

20   temperature being kept below 155°C. After the acid number had fallen to less than 3 mg of KOH/gram of resin, the resin was cooled.

      Viscosity according to the falling ball method: 44 dPa.s (65% solid in propyleneglycolmonomethylether acetate,

25   23°C).

      The resin properties of the products obtained after the various synthesis steps are shown in Table I.

Table I

30

Example	I	II	III	IV
Generation	1	2	3	4
Mn (theoretical)	2210	6360	14670	31275
Acid number	2.9	1.2	0.9	1.1
Viscosity (65% solid in propylene glycol monomethyl ether acetate)	5.5	11	21.5	44

40

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The viscosity (in dPa.s) was determined (at 23°C) according to the falling ball method (Noury-v.d. Lande).

5   The acid number (mg of KOH/gram of resin) was determined by titration with an ethanolic potassiumhydroxide solution. (PC) = 0.855.

Examples V-VIII

10 Preparation of hyperbranched polyester

Example V (1st generation)

In a 1.5-litre glass pressure reactor having a mechanical stirrer and a thermometer, 100 grams of

15 trimethylolpropane (0.75 mol), ·432 grams of trimelliticacidanhydride (2.25 mol) and 345 grams of propyleneglycolmonomethyletheracetate were warmed to 140°C, after which the temperature was kept at 140°C for 30 minutes. After cooling to 120°C, 0.2% by weight of

20 dimethylbenzylamine was added, after which 274 grams of propylene oxide (4.5 mol + 5% by weight excess) were metered in, with the temperature being kept below 125°C. After the acid number had fallen to less than 4 mg of KOH/gram of resin, 34 grams of propyleneglycolmonomethyletheracetate

25 were added and the resin was cooled.

Viscosity according to the falling ball method: 11 dPa.s (65% solid in propyleneglycolmonomethyletheracetate, 23°C).

30 Example VI (2nd generation)

In a 1.5-litre glass pressure reactor having a mechanical stirrer and a thermometer, 436 grams of the product (0.28 mol of solid resin) obtained in generation 1, 323 grams of trimelliticacidanhydride (1.68 mol) and 208

35 grams of propyleneglycolmonomethyletheracetate were warmed to 130°C, after which the temperature was kept at 130°C for 30 minutes. After cooling to 120°C, 0.2% by weight of dimethylbenzylamine was added, after which 214 grams of propyleneoxide (3.36 mol + 10% excess) were metered in,

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with the temperature being kept below 125°C. After the acid
number had fallen to below 4 mg of KOH/gram of resin, 40
5 grams of propyleneglycolmonomethyletheracetate were added
and the resin was cooled.

Viscosity according to the falling ball method: 27
dPa.s (65% solid in propyleneglycolmonomethyletheracetate,
23°C).
10

Example VIII (3rd generation)
In a 1.5-litre glass pressure reactor having a
mechanical stirrer and a thermometer, 548 grams of the
product (0.13 mol of solid resin) obtained in generation 2,
15 300 grams of trimelliticacidanhydride (1.56 mol) and 193
grams of propyleneglycolmonomethyletheracetate were warmed
to 135°C, after which the temperature was kept at 135°C for
30 minutes. After cooling to 120°C, 0.2% by weight of
dimethylbenzylamine was added, after which 199 grams of
20 propyleneoxide (3.12 mol + 10% excess) were metered in, with
the temperature being kept below 125°C. After the acid
number had fallen to below 4 mg of KOH/gram of resin, 38
grams of propyleneglycolmonomethyletheracetate were added
and the resin was cooled.
25   Viscosity according to the falling ball method:
59 dPa.s (65% solid in propyleneglycolmonomethylether-
acetate, 23°C).

Example VIII (4th generation)
30   In a 1.5-litre glass pressure reactor having a
mechanical stirrer and a thermometer, 549 grams of the
product (0.057 mol of solid resin) obtained in generation 3,
263 grams of trimelliticacidanhydride (1.37 mol) and 142
grams of propyleneglycolmonomethyletheracetate were warmed
35 to 135°C, after which the temperature was kept at 135°C for
30 minutes. After cooling to 120°C, 0.2% by weight of
dimethylbenzylamine was added, after which 175 grams of
propyleneoxide (2.74 mol + 10% excess) were metered in, with
the temperature being kept below 125°C. After the acid

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number had fallen to below 4 mg of KOH/gram of resin, 55
grams of propyleneglycolmonomethyletheracetate were added
5 and the resin was cooled.

Viscosity according to the falling ball method:
104 dPa.s (65% solid in propyleneglycolmonomethylether-
acetate, 23°C).

The resin properties of the products obtained after
10 the various synthesis steps are shown in Table II.

Table II

Example	V	VI	VII	VII
15 Generation	1	2	3	4
Mn (theoretical)	1060	2910	6600	14000
Acid number	3.9	2.5	3.0	3.8
20 Viscosity (65% solid in				
propylene glycol	11	27	59	104
monomethyl ether				
acetate)				

25

The viscosity (in dPa.s) was determined, at 23°C,
according to the falling ball method.

The acid number (mg of KOH/gram of resin) was
determined by titration with an ethanolic potassiumhydroxide
30 solution.

Examples IX-XIV

Example IX (1st generation)
35   In a 1-litre glass reactor having a mechanical
stirrer and a thermometer, 225 grams of trimethylolpropane
(1.68 mol) and 504 grams of succinicacidanhydride (5.04 mol)
were warmed to 110°C in a nitrogen atmosphere. After a few
minutes the temperature was raised to 150°C and kept at

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that temperature for 3 hours. After cooling, the acid-number
of the obtained first generation product (A) was determined:
399 mg KOH/gram. The viscosity was 31 mPa.s (Emila, 50% in
methylisobutylketone, 23°C). M_n (theoretical) = 434.
Polydispersity: 1.2-1.3.

Example X (1st generation)

In a 1-litre glass reactor having a mechanical
stirrer and a thermometer, 214 grams of (A), 387 grams
Cardura E10™ (1.52 mol) and 0.1 gram dimethylaminopyridine
were warmed to 150°C in a nitrogen atmosphere. The
temperature was kept at 150°C until the acid-number was
lower than 3 mg KOH/gram. After cooling, the hydroxy-number
of the obtained first generation product (B) was determined:
132 mg KOH/gram. The acid-number was 0.7 mg KOH/gram. The
viscosity was 11 mPa.s (Emila, 50% in methylisobutylketone,
23°C). Mn (theoretical) = 1191. Polydispersity: 1.3-1.7.

Example XI (2nd generation)

In a 1-litre glass reactor having a mechanical
stirrer and a thermometer, 229 grams of (B), 103 grams of
trimellitic acid anhydride (0.54 mol), 332 grams of
methylisobutylketone and 0.1 grams dimethylaminopyridine
were warmed to 100°C in a nitrogen atmosphere and kept at
that temperature for 5 hours. After cooling, the acid-number
of the obtained second generation product (C) was
determined: 189 mg KOH/gram. The viscosity was 43 mPa.s
(Emila, 50% in methylisobutylketone (MIBK), 23°C). Mn
(theoretical) = 1775. Polydispersity 1.4-2.4.

Example XII (2nd generation)

In a 1-litre glass reactor having a mechanical
stirrer and a thermometer, 199 grams of (C), 90 grams
Cardura E10™ (0.35 mol) and 0.1 gram dimethylaminopyridine
were warmed to 150°C in a nitrogen atmosphere. The
temperature was kept at 150°C during 2 hours, while the loss
of MIBK was destilled off. At the moment the acid-number was

lower than 3 mg KOH/gram the product (D) was cooled and the
MIBK was added again. The hydroxy-number of the obtained

5   second generation product (D) was determined: 116 mg
KOH/gram. The acid-number was 0.3 mg KOH/gram. The viscosity
was 23 mPa.s (Emila, 50% in methylisobutylketone, 23°C). Mn
(theoretical) = 3245. Polydispersity 1.8-3.2.

10   Example XIII (3rd generation)
        In a 1-litre glass reactor having a mechanical
stirrer and a thermometer, 176 grams of (D), 48.5 grams of
trimellitic acid anhydride (0.25 mol), 117 grams of
methylisobutylketone and 0.05 grams dimethylaminopyridine

15   were warmed to 100°C in a nitrogen atmosphere and kept at
that temperature for 6 hours. After cooling, the acid-number
of the obtained third generation product (E) was determined:
157 mg KOH/gram. The viscosity was 87 mPa.s (Emila, 50% in
methylisobutylketone, 23°C). Mn (theoretical) = 4397.

20   Polydispersity: 2.2-3.2.

     Example XIV (3rd generation)
        In a 1-litre glass reactor having a mechanical
stirrer and a thermometer, 230 grams of (E), 101.6 grams

25   Cardura E10™ (0.40 mol) and 0.1 gram dimethylaminopyridine
were warmed to 150°C in a nitrogen atmosphere. The
temperature was kept at 150°C during 2 hours, while the loss
of MIBK was destilled off. At the moment the acid-number was
lower than 3 mg KOH/gram the product (F) was cooled and the

30   MIBK was added again. The hydroxy-number of the obtained
third generation product (F) was determined: 112 mg
KOH/gram. The acid-number was 0.6 mg KOH/gram. The viscosity
was 62 mPa.s (Emila, 50% in methylisobutylketone, 23°C). Mn
(theoretical) = 7457. Polydispersity: 3.1

35

While the invention has been described in detail and with
reference to specific embodiments thereof, it is apparent to
one skilled in the art that various changes and
modifications can be made therein without departing from the

40   spirit and scope thereof.

<u>Examples XV-XVIII</u>

Preparation coating composition.

The products obtained in the Examples I, II, III
and IV are used in the following coating compositions
(respectively Examples XV to XVIII):

83.33 parts by weight of the product obtained

14.71 parts by weight hexamethoxymethylmelamine

1.96 parts by weight p-toluenesulfonicacid (Dynapol
                      Catalyst 1203, Hüls).

The obtained coating compositions were mixed with
propyleneglycolmonomethyletheracetate until a solid content
of 62% was reached. Next, a 100 μm film was made of these
polymer compositions using an Erichsen filmforming apparatus
(type 360, width 60 mm) on a glass or steel surface. A
curing cycle of 5 minutes at 200°C was used. The mechanical
properties of the films obtained are given in the following
table III:

<u>Table III</u>

Example coating composition	XV	XVI	XVII	XVIII
elasticity (mm)	5.5	7	8	8
reverse impact (inch/lb)	20	20	80	60
König hardness (sec)	63	137	123	106
acetone-resistivity (dR)	>100	>100	>100	>100

The elasticity is determined according to DIN 53156.
The reverse impact is determined according to ASTM-D-2794.
The König hardness is determined according to DIN 53157.

Example XIX

          A composition was made using:

5   27.01 parts by weight of the product obtained in Example
     III,
     27.01 parts by weight Uralac XP 970 SH (solid resin, high
     molecular weight polyester, Mn 15000),
     45.98 parts by weight propyleneglycolmonomethyletheracetate.

10   The viscosity of this polymer composition was 45
     dPa.s (23°C, 54% solid).

Example XX

          A composition was made using:

15   11.49 parts by weight of the product obtained in Example
     III,
     34.48 parts by weight Uralac XP 970 SH (solid resin, high
     molecular weight polyester, Mn 15000),
     54.02 parts by weight propyleneglycolmonomethyletheracetate.

20   The viscosity of this polymer composition was 11.5
     dPa.s (23°C, 46% solid).

Examples XXI and XXII

          The products obtained in the Examples XIX and XX

25   are used in the following coating compositions (respectively
     Examples XXI and XXII):
     83.33 parts by weight of the product obtained
     14.71 parts by weight hexamethoxymethylmelamine
      1.96 parts by weight p-toluenesulfonicacid (Dynapol

30   Catalyst 1203, Hüls).

          From the obtained coating compositions a 100 μm
     film was made of these polymer compositions using an
     Erichsen filmforming apparatus (type 360, width 60 mm) on a
     glass or steel surface. A curing cycle of 5 minutes at 200°C

35   was used. The mechanical properties of the films obtained
     are given in the following table IV:

- 18 -

Table IV

Example coating composition	XXI	XXII
elasticity (mm)	8	8
reverse impact (inch/lb)	160	160
König hardness (sec)	150	218
acetone-resistivity (dR)	40	40

The elasticity is determined according to DIN 53156.
The reverse impact is determined according to ASTM-D-2794.
The König hardness is determined according to DIN 53157.

C L A I M S

5   1.   Hyperbranched polymer comprising a nucleus and polyol
         and polycarboxy residues, the hyperbranched polymer
         having at least 6 terminal hydroxyl- or carboxyl groups
         and a Carothers gelpoint lower than 1.
    2.   Hyperbranched polymer according to claim 1,
10   characterized in that the hyperbranched polymer has at
         least 8 terminal hydroxyl- or carboxyl-groups.
    3.   Hyperbranched polymer according to claim 1,
         characterized in that the Patton-index is lower than
         0.95.
15   4.   Hyperbranched polymer having at least 6 terminal
         hydroxyl- or carboxylgroups obtainable by starting with
         a nucleus compound containing at least one hydroxyl
         group as the nucleus and reacting it with a compound
         containing at least one anhydride group, after which the
20   resulting first generation acid-terminated addition
         product is reacted with a compound containing at least
         one epoxy group; the resulting first generation
         hydroxyl-terminated addition product thereafter is
         reacted, in the second generation, with a compound
25   containing at least one anhydride group, after which the
         resulting second generation acid-terminated addition
         product, is reacted with a compound containing at least
         one epoxy group, resulting in a second generation
         hydroxyl-terminated addition product, and in at least
30   one generation monomers are used that have at least one
         functional group besides the anhydride group or epoxy
         group.
    5.   Hyperbranched polymer according to claim 4,
         characterized in that the hyperbranched polymer has 1-20
35   generations.
    6.   Hyperbranched polymer according to one of claims 4-5,
         characterized in that the nucleus is formed by the
         addition reaction of a compound containing at least one
         carboxyl group and a compound containing at least one
40   epoxy group.

7. Hyperbranched polymers according to one of claims 4-6, characterised in that the nucleus contains 1-10 hydroxyl groups.

8. Hyperbranched polymers according to one of claims 4-7, characterized in that the nucleus is a low molecular weight polyol.

9. Hyperbranched polymer according to one of claims 4-8, characterized in that the compound containing at least one anhydride group is trimellitic acid anhydride.

10. Hyperbranched polymer according to one of claims 4-9, characterized in that the compound containing at least one epoxy groups is a monoepoxide.

11. Process for the preparation of a hyperbranched polymer, characterised in that a nucleus compound containing at least one hydroxyl group is reacted with a compound containing at least one anhydride group, after which the resulting first generation acid-terminated addition product is reacted with a compound containing at least one epoxy group; the resulting first generation hydroxyl-terminated addition product thereafter is reacted, in the second generation, with a compound containing at least one anhydride group, after which the resulting second generation acid-terminated addition product, is reacted with a compound containing at least one epoxy group, resulting in a second generation hydroxyl-terminated addition product, and in at least one generation monomers are used that have at least one functional group besides the anhydride group or epoxy group.

12. Process according to claim 11, characterised in that the molar ratio between the terminal hydroxyl groups and the anhydride groups containing compounds or between the terminal acid groups and the epoxy groups containing compounds is about 1.1:0.9 to 0.9:100.

13. Process according to one of claims 11-12, characterised in that the temperature during the various reactions is between 80°C and 160°C.

14. Use of hyperbranched polymers according to one of claims
    1-10 or use of hyperbranched polymers obtained according
5   to one of claims 11-13 in coating compositions.

15. Polymer, process and use, substantially as described in
    the description and the examples.

INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER   (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.5   C 08 G   63/12   C 08 G   63/42   C 09 D 167/00

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl.5	C 08 G

Documentation Searched other than Minimum Documentation
to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]		
Category[o]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
X	US,A,3459733 (W.M. BYRD, Jr. et al.) 5 August 1969, see column 1, line 36 - column 3, line 37; examples 9,12-14 ---	1,2,4-8 ,10-13
X	GB,A, 934782 (STANDARD OIL CO.) 21 August 1963, see claims 1-3,8,9,14; example 1 ---	1,14
X	Chemical Abstracts, vol. 108, no. 20, 16 May 1988, (Columbus Ohio, US), see abstract no. 168606z, & JP,A,62207318 (ASAHI GLASS CO.) 11 September 1987, see registry no. 112408-92-1; abstract --- -/-	1

° Special categories of cited documents :[10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION	
Date of the Actual Completion of the International Search 28-06-1993	Date of Mailing of this International Search Report 0 5. 08. 93
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer D.H. KRISCHE

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT   (CONTINUED FROM THE SECOND SHEET)

Category°	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
Y	H.F. MARK et al., "Encyclopedia of Polymer Science and Engineering", index volume, 1990, John Wiley & Sons, New York, US, page 46, D.A. TOMALIA et al.: "Dendritic polymers", see pages 60-61,64-65 (cited in the application) ---	1,2,4-13,15
Y	US,A,4659778 (R.C. WILLIAMS) 21 April 1987, see claims 7-15; examples A,I,K; column 10, line 13 - column 11, line 7	1,2,4-13,15
Y		1,2,4-15
Y	US,A,4568737 (D.A. TOMALIA et al.) 4 February 1986, see column 2, line 40 - column 3, line 32; column 8, line 49 - column 9, line 15 -----	1,2,4-15

ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.

NL 9300051
SA   71616

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report.
The members are as contained in the European Patent Office EDP file on 27/07/93
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
US-A- 3459733	05-08-69	BE-A-	670904	31-01-66
		CH-A-	478081	15-09-69
		DE-A-	1493110	11-11-71
		FR-A-	1475671	
		GB-A-	1129096	
		NL-A-	6513367	18-04-66
GB-A- 934782		None		
US-A- 4659778	21-04-87	AU-B-	596653	10-05-90
		AU-A-	7144187	22-10-87
		BE-A-	1001614	19-12-89
		CA-A-	1279433	22-01-91
		DE-A-	3713080	29-10-87
		FR-A-	2597490	23-10-87
		GB-A,B	2189497	28-10-87
		JP-A-	62256824	09-11-87
		NL-A-	8700922	16-11-87
		US-A-	4743655	10-05-88
		US-A-	4789706	06-12-88
US-A- 4568737	04-02-86	US-A-	4507466	26-03-85
		US-A-	4587329	06-05-86
		AU-B-	560604	09-04-87
		AU-A-	2435484	02-08-84
		CA-A-	1244586	08-11-88
		EP-A-	0115771	15-08-84
		WO-A-	8402705	19-07-84
		US-A-	4558120	10-12-85
		US-A-	4631337	23-12-86
		US-A-	4737550	12-04-88